

Spin-orbit Coupling Effects on the Electronic Structure of UO_2

Lindsay E. Roy, Richard L. Martin, T-12; Tomasz Durakiewicz, John J. Joyce, MPA-10; Gustavo Scuseria, Rice Univ.

The corrosion reactions of uranium and transuranic metals pose a serious concern for environmental preservation. The long-term storage of radioactive waste (containing mainly uranium and plutonium compounds) requires a comprehensive knowledge of the possible oxidation reactions that could occur. These materials also represent a challenge for theorists; materials belonging to this class usually have partially occupied f orbitals where the electrons compete between itinerancy and localization.

When localized, the f electrons are strongly correlated, and these interactions normally lead to Mott-Hubbard insulators. For example, plutonium crystallizes in seven distinct phases, is highly reactive, and can have five different oxidation states when forming compounds. The surface of metallic plutonium easily oxidizes to PuO_2 when exposed to air and moisture, while Pu_2O_3 plays an important role in oxidation kinetics.

Given the incomplete understanding of the Pu oxidation chemistry and the myriad problems associated with experimental studies on these materials, theory can provide fundamental insight into the electronic structure and properties of these systems. Unfortunately, theoretical studies on these materials are quite difficult. The $5f$ electrons can either be localized or contribute to bonding, and their relativistic effects and electron-electron correlations are very important factors in deciding the degree of localization. In particular, actinide oxides (AnO_2) exhibit amazingly complex behavior, despite having a simple binary formula, because they straddle the metallic, ionic, and covalent bonding descriptions used by chemists and physicists. Most of these oxides are small band gap insulators and some exhibit antiferromagnetic ordering, or have uncertain magnetic ordering, at low temperature. Because of the strong correlations, previous theoretical studies on these materials using local spin-density approximation (LSDA) and generalized gradient approximations (GGA) of density functional theory (DFT) fail to accurately describe the bonding and electronic structure of these compounds.

Recently, we have shown that a third generation of functionals, the hybrid DFT approximation that combines the exact, non-local, Hartree-Fock exchange interaction with the traditional local (LDA) or semi-local GGA exchange and correlation interactions, is able to correctly predict a magnetic ground state, the insulating gap, and the lattice constants for UO_2 series. In addition, the $5f$ orbitals are nearly localized in the band structure of UO_2 , but there is a small dispersion of ~ 300 meV. This dispersion has recently been verified by colleagues in MPA-10.

We have recently included the effect of spin-orbit coupling (SOC), or the interaction of the electron spin magnetic moment with the magnetic moment due to the orbital motion of the electron, in our calculations. Our work on UO_2 with SOC shows that the band gap decreases by only 0.06 eV, and that SOC is a minor perturbation. We are currently working on including SOC effects in the entire AnO_2 series.

For further information contact Lindsay E. Roy at lroy@lanl.gov.

Funding Acknowledgments

- Department of Energy, Office of Science, Office of Basic Energy Sciences

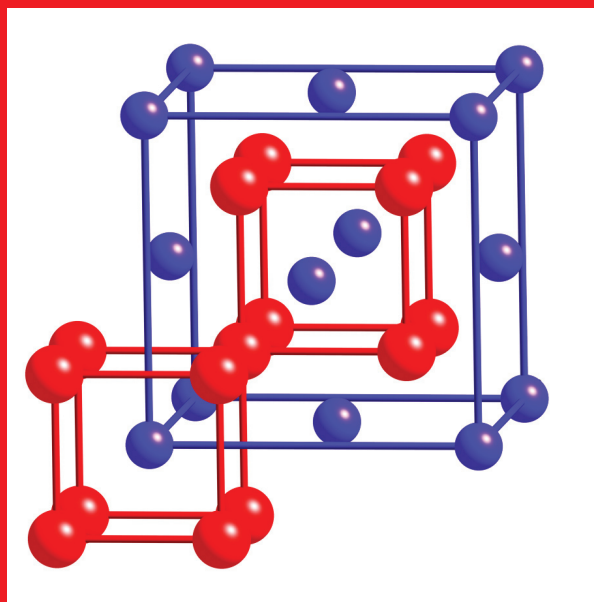


Fig. 1. The CaF_2 -like lattice of actinide dioxides. The actinide and oxygen atoms form face-centered and simple cubic sublattices, respectively. Actinide and oxygen sites are in blue and red, respectively.

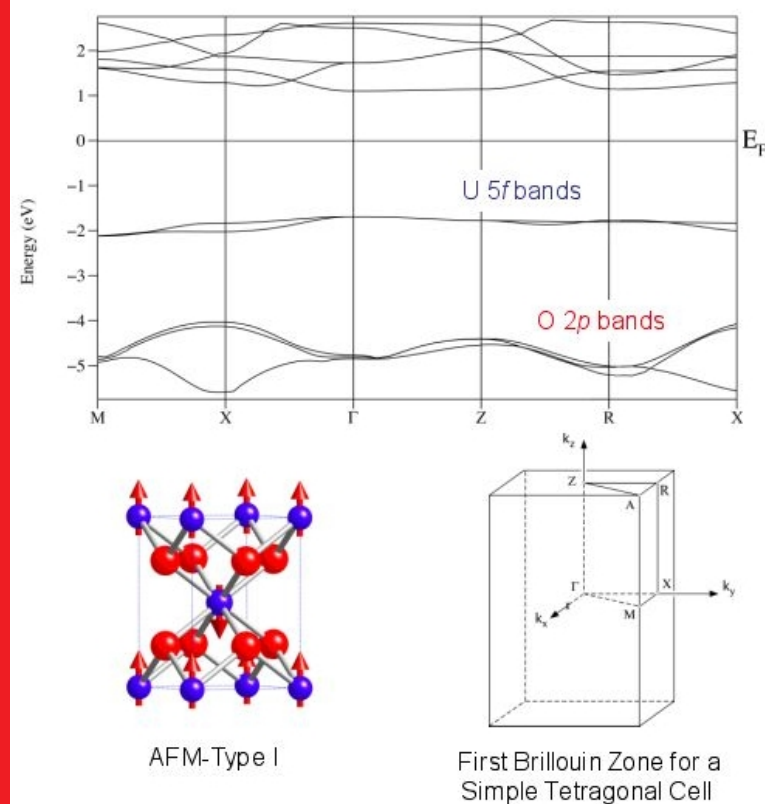


Fig. 2. Alpha-spin band structure of the antiferromagnetic UO_2 structure (AFM-Type I). The antiferromagnetic cell used in the calculation is a subgroup of the face-centered cubic UO_2 structure. The red arrows represent the direction of the $5f^2$ electrons on each uranium atom. The first Brillouin zone with the proper indexing of the relevant points for a simple tetragonal cell is also shown. One can see that the oxygen p bands are well separated from the uranium f bands and that the occupied 5f bands show some dispersion and have a bandwidth of ~ 300 meV.